DEFENCE RESEARCH BOARD OF CANADA
IN ASSOCIATION WITH
DEPARTMENT OF MECHANICAL ENGINEERING
UNIVERSITY OF TORONTO

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

X. THE CAUSE OF PREIGNITION (SURFACE IGNITION) OF UNDOPED LIQUID FUEL

By R. O. King and E. J. Durand

DEFENCE RESEARCH BOARD
1950
From
Acc. No.
Ch. of Copies

Reprinted from
CANADIAN JOURNAL OF RESEARCH
Vol. 27, Sec. A, 1949

106-04308/

Reprinted from Canadian Journal of Research, F, 27 : 337-348. September, 1949

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

X. THE CAUSE OF PREIGNITION (SURFACE IGNITION)—UNDOPED LIQUID FUEL[1]

BY R. O. KING[2] AND E. J. DURAND[3]

Abstract

The theory is advanced that surface ignition, generally described as preignition, if occurring during compression, is due to partial oxidation of the fuel to aldehyde, a relatively small concentration of this inflammable substance being sufficient for ignition of the charge by the hot surfaces normally present in the combustion space of a high duty engine. The igniting effect may be early or late, that is, before or after spark ignition. Early surface ignition may cause destruction of pistons and exhaust valves of supercharged engines and is indicated by severe knocking. When the effect occurs late in the combustion period there is no destructive effect and the engine will run without spark ignition. The theory is confirmed by engine experiments with rich mixtures which oxidize readily to aldehyde, and it is shown that the occurrence of surface ignition then depends on surface and mixture temperatures. Thus in temperature conditions chosen to eliminate surface ignition, *n*-heptane can be used in the C.F.R. engine at 10 : 1 compression ratio and the performance of acetaldehyde does not differ from that of a hydrocarbon fuel. A conclusion of importance in practice is that early surface ignition may occur in a particular cylinder of a multicylinder supercharged engine receiving an extremely rich mixture, because of uneven distribution. If the surface ignition led to the destruction of an exhaust valve or a piston, continued running of a highly supercharged engine on the unaffected cylinders would have the disastrous consequences arising from explosion of the compressed mixture in the induction system.

Introduction

An essential condition of the type of knocking combustion frequently described as "detonation" is that the end gas be in a chemical or physical state such that flame propagation can occur in it at an abnormally high rate, otherwise combustion, already proceeding at normal velocity, would be completed without knock. It is held generally that the presensitization of the end gas is due to preflame oxidation reactions. On the other hand, according to the hypothesis advanced in Part IV (10), an abnormally high rate of flame propagation is a consequence of the end gas having become impregnated with finely divided carbon. The carbon is provided by pyrolysis of the lubricating oil when hydrogen or town gas is used as engine fuel, as demonstrated experimentally, Parts V (13) and VI (14), but mainly by pyrolysis of the fuel when liquid hydrocarbons are used.

Abnormally rapid combustion of the presensitized end gas might occur by sudden acceleration of the normal rate of flame movement as in long tubes; in the

[1] *Manuscript received in original form March 5, 1949, and, as revised, June 8, 1949.*
Contribution from Defence Research Board, Ottawa, Canada, in association with the Department of Mechanical Engineering, University of Toronto.
[2] *Research Scientist, Naval Division, Defence Research Board and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto. Lately Director of Scientific Research and Development, Royal Canadian Navy.*
[3] *Lecturer, Mechanical Engineering, University of Toronto.*

engine combustion space the effect can be initiated by nuclei acting as promoters of ignition or by the igniting effect of hot surfaces. Both types of ignition are shown by the high speed photographs of knocking combustion taken by Withrow and Rassweiler (21). The phenomena are shown even more distinctly by the ultra high speed photographs taken by Miller (17) and by Miller, Olsen, Logan, and Osterstrom (18).

Surface ignition, unlike the nuclear type, need not be confined to the end gas and may occur at any time after the opening of the inlet valve and is described loosely as preignition. The term would better be applied to induction ignition which seldom occurs unless initiated by the residual flame of slow burning mixtures. The term "surface ignition" is therefore applied to an igniting effect arising after the closing of the inlet valve.

When surface ignition occurs before optimum ignition timing, it is equivalent to advancing the spark and will be described as "early". When it occurs after optimum ignition timing, it is equivalent to retarding the spark and will be described as "late". The engine will continue to run on late surface ignition when spark ignition is switched off.

"Preignition" is commonly believed to be due to the igniting effect of incandescent spark plug points or patches of carbonaceous or other matter in respect of the combustible mixture as admitted to the engine cylinder. Induction ignition is possible accordingly but not the surface ignition which occurs especially when using rich mixtures after the inlet valve closes and the "hot points" have been cooled by the entering charge. Incidentally, methanol is exceptionally prone to surface ignition in spite of the cooling effect due to the high latent heat of vaporization. Thus an increase in the inflammability of the combustible mixture during compression in combination with suitable temperatures appeared to be required for promotion of surface ignition.

An increase of inflammability would be obtained on the partial oxidation of the hydrocarbon fuel to aldehyde which is known to occur during compression, and whether or not ignition then occurred would depend on the concentration of aldehyde attained and on maximum surface temperature which can be controlled, especially in a liquid cooled engine. The engine experiments to be described were planned accordingly, it being assumed as indicated by the experiments of Part II (8) that aldehyde is formed by a heterogeneous oxidation reaction and that ignition of the substance is not autocatalytic.

Experimental Arrangements

The standard C.F.R. engine was used for the experiments. Richer mixtures than usual were obtained as required by using oversize fuel flow control orifices. Knock intensity described as "standard" is defined in Part VIII (12, p. 215) and is somewhat lighter than the A.S.T.M. standard.

The fuels used for the experiments were as follows,—

Fuel S, Lot 1: Distillation range 85° to 429°F. See graph of Fig. 1, Part VIII (12), for details.

n-Pentane: technical grade, initial boiling point 94°F., dry point 100°F.

n-Hexane: commercial grade, initial boiling point 150°F., dry point 156°F.

n-Heptane: as supplied for octane number determination according to C.F.R.–A.S.T.M. procedures; boiling point closely approximates the correct value of 98.38°C. (209°F.).

Acetaldehyde: pure, boiling point, 21°C. (70.8°F.).

Preliminary Engine Experiments with the Three Paraffins and Fuel *S*

Temperatures of initial oxidation or combustion of pentane, hexane, and heptane taken as indicated by the appearance of peroxides, aldehyde, water,

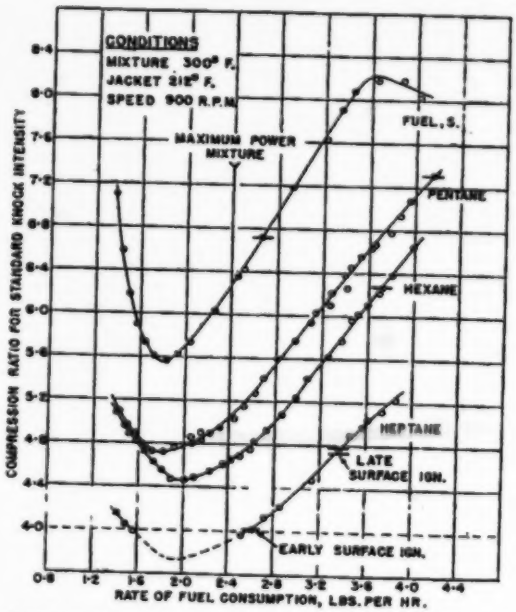

FIG. 1. *Effect of mixture enrichment on the combustion of heptane, hexane, pentane and fuel S in the engine.*

and carbon oxides in the reaction products, are given by Pye (20, p. 98) as 295°, 266°, and 230°C. respectively. The given values are regarded as approximate only, mixture strength not having been closely controlled.

Preliminary engine experiments using the three paraffins mentioned and fuel *S* were made in high temperature operating conditions, mixture strength

being continuously enriched to promote surface ignition while compression ratio was increased to maintain standard knock intensity. Ignition timing was retarded as compression ratio was increased, in accordance with the C.F.R.–A.S.T.M. method of knock rating. The results of the experiments are given by the graphs of Fig. 1.

The beginning of early surface ignition is marked on the graphs by single short horizontal lines. It will be noted, as would be expected from the consideration mentioned above, that the effect occurred at decreasing mixture strength and decreasing temperature as represented by usable compression ratio, as the paraffin series was ascended from pentane to heptane.

Late surface ignition on which the engine would run without spark ignition is indicated by the pair of short horizontal lines on the graph for heptane. The effect was obtained with that fuel only. There were indications of early surface ignition when rates of heptane supply were even lower than those indicated on the graph as marking the beginning of the effect. The occasional surface ignition knock then obtained was "heavy", as would be expected. On the other hand, the late surface ignition knock observed when the engine would run without spark ignition was nearly continuous, and intensity differed so little from that adopted as "standard" that it was necessary to switch off the spark ignition to demonstrate the existence of the effect.

Cool Engine Experiments with Heptane

The preliminary experiments indicated that heptane was the most suitable fuel to use for engine experiments to be made in conditions adapted to eliminate combustion knock due to either early or late surface ignition. Further experiments were made, therefore, with the temperature of the jacket cooling water, taken at the outlet, reduced to 100°F., the heptane–air mixture unheated, and the engine speed reduced to 400 r.p.m. to reduce power and consequently the temperature gradient from the combustion space surface to the coolant. The experimental results are given by Graph *A* of Fig. 2. A second set of experiments was made in similar temperature conditions but with the engine speed raised to 900 r.p.m. The results are given by Graph *B* of the figure. Graph *C* of the figure for the heptane as used in standard C.F.R.–A.S.T.M. knock testing conditions is reproduced from Fig. 1 to show the remarkable change in performance obtained on eliminating surface ignition.

There was not the slightest indication of early or late surface ignition during the low temperature experiments, at either 400 or 900 r.p.m. At 400 r.p.m. standard knock intensity could be maintained at compression ratios rising from 4.55 to 10:1 as the rate of heptane supply was increased from 1.3 to 2.1 lb. per hr., which represents an increase in mixture strength of 62%. At 900 r.p.m. standard knock intensity could be maintained as compression ratio was raised from the minimum value of 5.3 to the measurement limit of 10, on increasing mixture strength by 50% only. It should be noted that the minimum

value of usable compression ratio is usually obtained at the "correct" mixture strength and that an increase of as much as 30% may be required to obtain maximum power.

The fuel performance obtained on the elimination of surface ignition is believed to be that governed by nuclear ignition of the end gas, and the de-

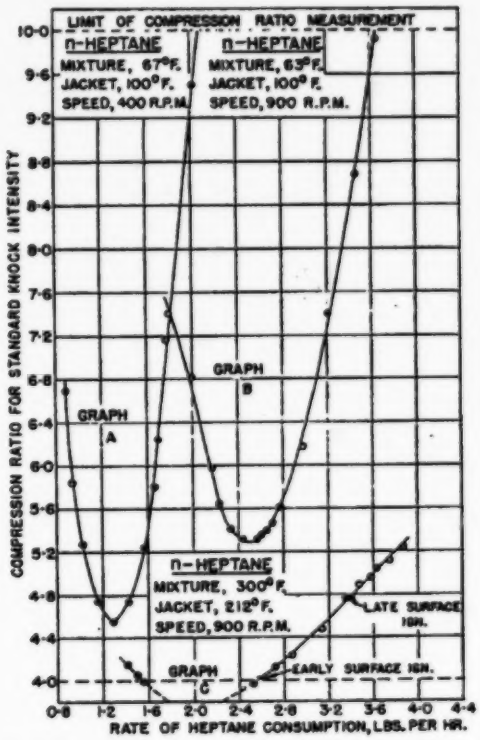

FIG. 2. *Effects of surface temperature and enrichment of the mixture on the combustion of heptane in the engine.*

crease of knock with increase of engine speed can then be attributed to the consequent decrease in the time available for pyrolysis of the fuel to yield the required concentration of finely divided carbon.

Engine Experiments with Acetaldehyde

Prettre (see W. Jost (7, p. 441)), discussing the luminescence of heated acetaldehyde–air mixtures, mentions that the lively combustion of the mixtures with a small surplus of aldehyde assumes an explosive form that is never observed in hydrocarbon–air mixtures and that normal ignition takes place at about 350°C. Egerton and Gates (2) obtained an igniting temperature of

395°C. on allowing a drop of acetaldehyde to fall into a heated iron pot; the igniting temperature of pentane was 515°C. in the same circumstances. It would be expected, therefore, that an acetaldehyde–air mixture would ignite prematurely if used in an engine as usually operated. Thus Egerton, Smith, and Ubbelohde (3, p. 464) state that the pure substance, b.p. 21°C., when used as fuel for an ethyl knock testing engine was "found to knock so violently that the engine could not be run".

It seemed to be possible, in the light of the experiments made with heptane, that the violent knock observed by Egerton *et al.* was due to early surface ignition and *not* to explosive combustion of the unburned mixture ahead of the flame, late in the combustion period.

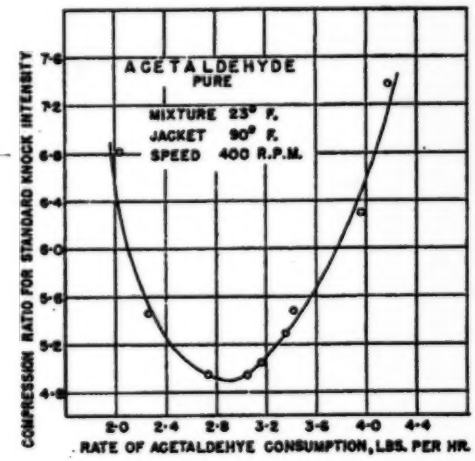

FIG. 3. *The antiknock effect of mixture enrichment when pure acetaldehyde is used as fuel for the C.F.R. engine.*

Experiments with the C.F.R. engine were carried out accordingly in conditions chosen to avoid surface ignition. The jacket cooling water was maintained at 90°F. and the engine run at 400 r.p.m. Furthermore, the experiments were delayed until mid-winter, when it was possible to reduce the laboratory air temperature to 55°F. The quantity of acetaldehyde available for the experiments was insufficient for a determination of the change of optimum ignition timing with change of compression ratio. A fixed ignition advance of 10° was chosen as suitable for a fast burning fuel.

The results of the engine trial are given graphically by Fig. 3. It will be seen that the acetaldehyde behaved like an ordinary hydrocarbon fuel. The minimum compression ratio, 4.9:1, with standard knock intensity was obtained when the rate of aldehyde supply was 2.9 lb. per hr. and standard knock intensity was maintained as rate of supply was increased until compression ratio

reached 7.4:1. The increase of mixture strength was then 48%, the rate of supply of 2.9 lb. per hr. being taken as corresponding to the "correct" mixture strength. The experiment was stopped at the compression ratio of 7.4:1 because frost then affected the flow from the carburetor jet; otherwise it might have been continued until the compression ratio reached the measurement limit of 10:1.

Discussion

The results of the engine experiments accord with the theory that ignition of liquid fuel during compression does not occur until the fuel has been partially oxidized to aldehyde. The results of laboratory experiments described in earlier Parts support the theory.

Thus it was shown by experiments, Part II (8), that pentane ignition temperatures as low as 515°C. and initial oxidation temperatures as low as 295°C. mentioned earlier can be obtained solely if experimental conditions are such that partial oxidation to aldehyde can occur. Turbulence was found to be the essential condition. Oxidation proceeded very slowly without that factor. Reaction was then to steam and carbon dioxide only and, in the absence of aldehyde, ignition could not be obtained even at 750°C., the limit of the indicating instrument. On the other hand, turbulence provided by convection currents in a vertical combustion tube sufficed to start oxidation at temperatures below 300°C., with profuse formation of aldehyde, Fig. 2, Part II, *loc. cit.*, and explosion occurred when the tube wall attained a temperature of 560°C.

The fuel–air mixture on passing the inlet valve of the engine, necessarily with great velocity, enters the hot cylinder and combustion space in a state of high turbulence, and the formation of aldehyde would be expected. The consequent tendency to surface ignition would not, according to the theory advanced, increase with increase of mixture strength unless rate of aldehyde formation increased accordingly. The combined effect of mixture enrichment and turbulence to increase rate of aldehyde formation was shown by experiments described in Part VII (11) using reaction chamber No. 10. The graphs relating to 25% weak, "correct", and 100% rich mixtures with air have been collected and are shown together, Fig. 4 of this Part. Air was supplied to the reaction chamber at 75 cc. per min. and pentane added as required for the stated mixture strengths. The graphs show that aldehyde is formed over the low temperature range at a rate increasing rapidly with increase of mixture strength. The maximum rate of low temperature oxidation, shown by the height of the "aldehyde hump" increased by more than 100% as mixture strength was increased from 25% weak to 100% rich, approximately the usable range in an engine. The fact that ignition did not occur is attributed to the rate of flow through the reaction chamber of 2.5 cc. volume being sufficiently rapid to remove the aldehyde almost immediately after formation.

There is, however, ample available experimental evidence respecting the formation of aldehyde during the compression of hydrocarbon air mixtures in

engines. Thus, Callendar *et al.* (1, p. 28) demonstrated the formation of aldehyde and peroxide during compression and obtained "auto-ignition and detonation" without spark ignition when using a rich mixture of undecane with air in a Ricardo E 35 engine, the mixture being preheated to 80°C. (176°F.) and the jacket water to the same temperature. Measurements were made later by Egerton, Smith, and Ubbelohde, (3, p. 460) of the aldehyde and

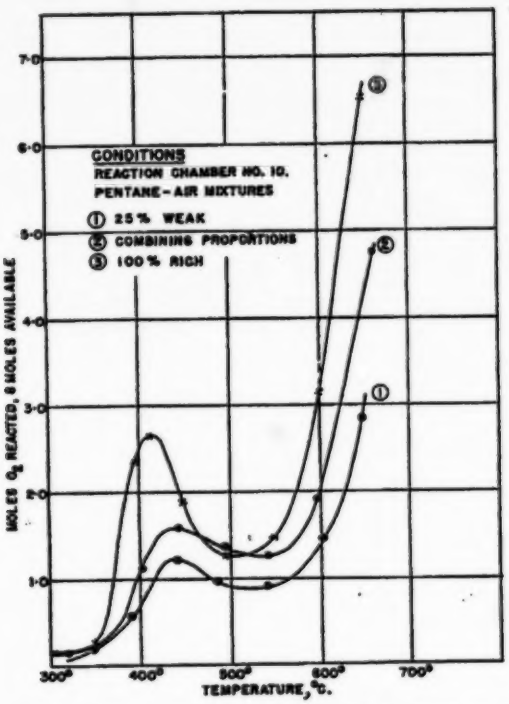

FIG. 4. *Oxidation reaction rates over "low" and "high" temperature ranges as affected by increase of mixture strength.*

peroxide formed during the compression stroke of an ethyl knock testing engine running at 600 r.p.m., using a jacket temperature 212°F. and unheated induction. Aldehyde was formed up to 10% by weight of the fuel although conditions in respect of mixture strength and temperature were not the most favorable. Moreover, although the engine was run under power, samples for aldehyde estimation were drawn only when spark ignition was switched off.

Concluding Comment

The conclusion arising from the experiments described in this Part, namely, that aldehyde is responsible for the preignition or surface ignition that occurs during compression, is novel, so far as known. The widely held view is that

the effect is due to the premature ignition of the fuel–air mixture, *in the state supplied to the engine*, by exceptionally hot spots in the combustion space such as spark plug points. Temperatures required are, according to Hundere and Bert (6), of the order of 2000°F. (1100°C.) for the first stages of preignition and several hundred degrees higher for very advanced preignition. They conclude that no material in the combustion space can attain the requisite temperatures without melting, other than the ceramic core of the spark plug, certain types of deposits, some from ethyl fluid, because of poor thermal contact with underlying surfaces and in some cases the exhaust valve head. Preignition occurs frequently, nevertheless, in ordinary motor car engines without surface temperatures rising to the degree required to melt an exhaust valve or an aluminum piston.

The usual method of determining preignition temperature is to heat a "temperature plug" projecting into the combustion space until ignition is obtained in advance of the spark. The extremely high "observed" plug temperature would be required unless the mixture contained excess fuel or constituents prone to oxidize to aldehyde. That is, temperatures of 2000°F. and over must have been observed in conditions in which preignition could not occur normally.

The adverse effect of uneven distribution of fuel–air mixtures to multicylinder engines, in respect of power developed, has long been recognized. Accurate measurements made by Gerrish and Meem (5) show differences in mixture strength as between cylinders of a multicylinder radial aero engine of as much as 30%, and Marble, Ritter, and Miller (16) describe methods of reducing the differences with the object of increasing the possible maximum power.

The experiments described in this Part show that it is important to provide for uniform distribution in order to avoid surface ignition, which, if occurring "early" in one cylinder of a supercharged engine, may have the disastrous consequences following from the burning of the exhaust valves and piston of that cylinder while the engine continues to run on the others.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. The cost of the work was defrayed in part by an Extramural Grant from the Defence Research Board (Canada). Assistance was given in the course of the work by Messrs. C. C. Li, E. H. Dudgeon, W. E. Morley, and H. W. M. Mar, all members of the staff of the Department of Mechanical Engineering, University of Toronto, and by Mr. H. Shanfield of the staff of the Department of Chemical Engineering.

References

1. CALLENDAR, H. L., KING, R. O., MARDLES, E. W. J., STERN, W. J., AND FOWLER, N. R. Aeronaut. Research Comm. Repts. & Mem. No. 1062. 1 26.
2. EGERTON, A. AND GATES, S. F. J. Inst. Petroleum Technol. 13 : 256-272. 1927.
3. EGERTON, A., SMITH, F. L., AND UBBELOHDE, A. R. Trans. Roy. Soc. (London), A, 234: 433-521. 1935.
4. GENCO, R. S. AND DRELL I. L. Nat. Advisory Comm. Aeronaut. Tech. Notes, 1618. 1948.
5. GERRISH, H. C. AND MEEM, J. L. JR. Nat. Advisory Comm. Aeronaut. Repts. 737. 1943. U.S. Government Printing Office, Washington 25, D.C.
6. HUNDERE, A., AND BERT J. A. Trans. Soc. Automotive Engrs. 2 : 546-562. 1948.
7. JOST, W. Explosion and combustion processes in gases. *Translated by* Huber O. Croft. McGraw-Hill Book Company Inc., New York and London. 1946.
8. KING, R. O. Can. J. Research, F, 26 : 36-56. 1948.
9. KING, R. O. Can. J. Research, F, 26 : 125-150. 1948.
10. KING, R. O. Can. J. Research, F, 26 : 228-240. 1948.
11. KING, R. O. Can. J. Research, F, 26 : 426-440. 1948.
12. KING, R. O., WALLACE, W. A., AND DURAND, E. J. Can. J. Research, F, 27 : 211-224. 1949.
13. KING, R. O., WALLACE, W. A., AND MAHAPATRA, B. Can. J. Research, F, 26 : 264-276. 1943.
14. KING, R. O., WALLACE, W. A., AND MAHAPATRA, B. Can. J. Research, F, 26 : 366-373. 1948
15. LORD, A. M., HEINICKE, O. H., AND STRICKER E. G. Nat. Advisory Comm. Aeronaut. Tech. Notes, 1617. 1948.
16. MARBLE, F. E., RITTER, W. K., AND MILLER, M. A. Nat. Advisory Comm. Aeronaut. Repts 821. 1945. U.S. Government Printing Office, Washington 25, D.C.
17. MILLER, C. D. Nat. Advisory Comm. Aeronaut. Repts. 855. 1946. U.S. Government Printing Office, Washington 25, D.C.
18. MILLER, C. D., OLSEN, H. L., LOGAN, W. O. JR., AND OSTERSTROM, G. E. Nat. Advisory Comm. Aeronaut. Repts. 857. 1946. U.S. Government Printing Office, Washington 25, D.C.
19. PETTY, D. S., WRIGHT, E. P., AND GARNER, F. H. Brit. Intelligence Objectives Subcomm., Final Rept. No. 1612. H.M. Stationery office, London.
20. PYE, D. R. The internal combustion engine. Vol. 1. Oxford University Press, London: Humphrey Milford. 1937.
21. WITHROW, L. AND RASSWEILER, S. M. Trans. Soc. Automotive Engrs. 31 : 297-304. 1936.